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(54) PLATINUM COMPLEX USEFUL AS SENSITIZER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a new metal complex having a high photoelectric transduction efficiency from a visible light, a dye-sensitization oxide semiconductor electrode using the metal complex and a solar battery comprising the electrode.

SOLUTION: This platinum complex is represented by general formula (1) PtL1L2 (1) [L1 is a ligand composed of a 2,2'-bipyridine-based compound containing at least one anionic group or a ligand composed of a 1,10- phenanthroline-based compound containing at least one anionic group; L2 is a dithitolate]. This dye-sensitization oxide semiconductor electrode is obtained by adsorbing the platinum complex on an oxide semiconductor film formed on an electroconductive surface. This solar battery is characterized by comprising the electrode, its counter electrode and a redox electrolyte to be brought into contact with the electrodes.

LEGAL STATUS

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* NOTICES *

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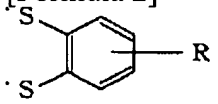
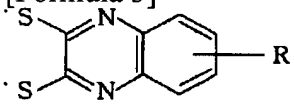
CLAIMS

[Claim(s)]
[Claim 1] The platinum complex expressed with the following general formula (1).
[Formula 1] PtL1L2 (1)
L1 shows among [type 1 containing the ligand or at least one anion radical which consists of a 2 and 2'-bipyridine system compound containing at least one anion radical, and the ligand which consists of a 10-phenanthroline system compound, and L2 is the following general formula (a).
[Formula 2]



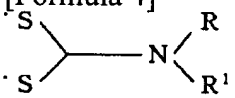
(a)

It is [whether it is expressed with (the alkoxyalkyl group in which R has the alkyl group of carbon numbers 1-6 and carbon numbers 1-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula), and] the following general formula (b).
[Formula 3]



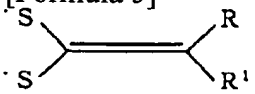
(b)

It is [whether it is expressed with (the alkoxyalkyl group in which R has the alkyl group of carbon numbers 1-6 and carbon numbers 1-12, the alumino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula), and] the following general formula (c).
[Formula 4]



(c)

It is expressed with (the alkoxyalkyl group in which R and R1 have the alkyl group of carbon numbers 1-6 and carbon numbers 1-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula), or is the following general formula (d).
[Formula 5]



(d)

the dithio rate expressed with (the alkoxyalkyl group in which R and R1 have the alkyl group of carbon numbers 1-6 and carbon numbers 1-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula) is shown --]
[Claim 2] The platinum complex expressed with the following general formula (2).
[Formula 6] PtLX1X2 (1)
L shows among [type 1 containing the ligand or at least one anion radical which consists of a 2 and 2'-

bipyridine system compound containing at least one anion radical, and the ligand which consists of a 10-phenanthroline system compound, and X1 and X2 are the same -- or -- differing -- **** -- the following general formula (e)

[Formula 7] **S-R [ ] e

or [being expressed with (the alkoxyalkyl group in which R has the alkyl group of carbon numbers 1-6, the alkenyl radical of carbon numbers 2-6, and carbon numbers 2-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula)] -- or the following general formula (f)

[Formula 8] - S-Ar (f)

It is] which shows the thio rate expressed with (Ar shows among a formula the aryl group which is not permuted [the permutation of carbon numbers 6-10, or]).

[Claim 3] The coloring matter sensitization oxide-semiconductor electrode which makes claim 1 or the platinum complex of 2 come to stick to the oxide-semiconductor film formed in the conductive front face.

[Claim 4] The solar battery characterized by consisting of the electrode and counter electrode of claim 3, and the redox electrolytic solution in contact with those electrodes.

[Translation done.]

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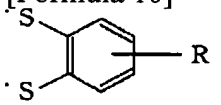
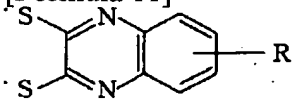
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the solar battery containing a platinum complex useful as a sensitizer which uses light energy efficiently, the coloring matter sensitization oxide-semiconductor electrode using this platinum complex, and this electrode.
[0002]
[Description of the Prior Art] Making compounds, such as a ruthenium complex which has absorption in the front face of oxide semiconductors, such as titanium oxide, in a visible region, adsorb, and raising the use effectiveness of light energy conventionally, using the sensitization is known. However, the compound used as a sensitizer until now was a metal complex which mainly has a ruthenium in a core.
[0003]
[Problem(s) to be Solved by the Invention] This invention makes it that technical problem to offer the solar battery containing the high new metal complex, the coloring matter sensitization oxide-semiconductor electrode using it, and this electrode of photoelectric conversion efficiency from the light.
[0004]
[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. That is, according to this invention, the platinum complex expressed with the following general formula (1) is offered.
[Formula 9] PtL1L2 (1)
L1 shows among [type 1 containing the ligand or at least one anion radical which consists of a 2 and 2'-bipyridine system compound containing at least one anion radical, and the ligand which consists of a 10-phenanthroline system compound, and L2 is the following general formula (a).
[Formula 10]



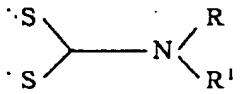
(a)

It is [whether it is expressed with (the alkoxyalkyl group in which R has the alkyl group of carbon numbers 1-6 and carbon numbers 1-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula), and] the following general formula (b).
[Formula 11]



(b)

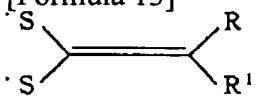
It is [whether it is expressed with (the alkoxyalkyl group in which R has the alkyl group of carbon numbers 1-6 and carbon numbers 1-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula), and] the following general formula (c).
[Formula 12]



(c)

It is expressed with (the alkoxyalkyl group in which R and R1 have the alkyl group of carbon numbers 1-6 and carbon numbers 1-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula), or is the following general formula (d).

[Formula 13]



(d)

the dithio rate expressed with (the alkoxyalkyl group in which R and R1 have the alkyl group of carbon numbers 1-6 and carbon numbers 1-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula) is shown --]
Moreover, according to this invention, the platinum complex expressed with the following general formula (2) is offered.

[Formula 14]

PtLX1X2 (1)

L shows among [type 1 containing the ligand or at least one anion radical which consists of a 2 and 2'-bipyridine system compound containing at least one anion radical, and the ligand which consists of a 10-phenanthroline system compound, and X1 and X2 are the same -- or -- differing -- **** -- the following general formula (e)

[Formula 15] **S-R [ ] e

or [being expressed with (the alkoxyalkyl group in which R has the alkyl group of carbon numbers 1-6, the alkenyl radical of carbon numbers 2-6, and carbon numbers 2-12, the amino alkyl group of carbon numbers 1-12, the alkoxy carbonyl of carbon numbers 1-6, and cyano ** show a hydrogen atom among a formula)] -- or the following general formula (f)

[Formula 16] - S-Ar (f)

It is] which shows the thio rate expressed with (Ar shows among a formula the aryl group which is not permuted [the permutation of carbon numbers 6-10, or]).

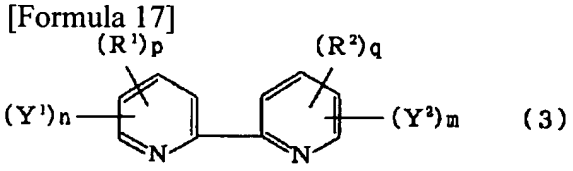
Furthermore, according to this invention, the coloring matter sensitization oxide-semiconductor electrode which makes said platinum complex come to stick to the oxide-semiconductor film formed in the conductive front face is offered. According to this invention, the solar battery characterized by consisting of said electrode, its counter electrode, and the redox electrolytic solution in contact with those electrodes is offered further again.

[0005]

[Embodiment of the Invention] L1 in said general formula (1) shows 1 containing the ligand or at least one anion radical which consists of a 2 and 2'-bipyridine system compound containing at least one anion radical, and the ligand which consists of a 10-phenanthroline system compound. Various kinds of well-known things, for example, a carboxyl group, a sulfonic group, a phosphoric-acid radical, etc. are conventionally included by said anion radical. These anion radicals can be free-acid radicals, and also can be neutralization bases neutralized with salt plasticity cations (ion of alkali metal, such as Na and K, ammonium ion, etc.). The one or more number of the anion radicals contained in a ligand L1 or L2 is two or more preferably, and the upper limit is usually about four. the sum total of the anion radical contained in L1, and the anion radical contained in L2 -- usually -- 1-4 -- it is 2 preferably.

[0006] What is general formula [following] (3) Shown in a said 2 and 2'-pyridine system compound is included.

[Formula 17]



(3)

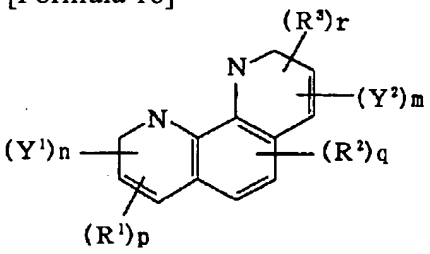
the inside of said formula, and Y1 and Y2 are the same -- or you may differ, an anion radical is shown

and R1 and R2 are the same -- or you may differ and a substituent is shown. The alkyl group of carbon numbers 1-4, a halogen atom (chlorine, a bromine, iodine, fluorine), the alkyl halide radical of carbon numbers 1-4, etc. are included by the substituent. n and m -- 0-4 -- desirable -- the number of 1-2 -- being shown -- n+m -- 1-6 -- 2 is shown preferably. p and q show the number of 0-6, and show the number of 0-2 preferably.

[0007] if the example of a said 2 and 2'-pyridine system compound is shown -- 2 and 2' - bipyridine - 4 and 4 - dicarboxylic acid, and '2, 2' -- the - bipyridine -4 and - disulfon acid, and 4 '2, 2'-bipyridine - 4 and 4 - JIRIN acid, and '2, 2' -- the - pyridine -3 and 3' -- the - dimethyl -4 and 4' - dicarboxylic acid (or a disulfon acid or a JIRIN acid) etc. is mentioned.

[0008] What is shown in said 1 and 10-phenanthroline system compound by the following general formula (4) is included.

[Formula 18]



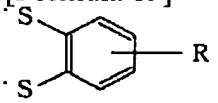
(4)

the inside of said formula, and Y1 and Y2 are the same -- or you may differ, an anion radical is shown and R1, R2, and R3 are the same -- or you may differ and a substituent is shown. The alkyl group of carbon numbers 1-4, a halogen atom (chlorine, a bromine, iodine, fluorine), the alkyl halide radical of carbon numbers 1-4, etc. are included by the substituent. n and m -- 0-4 -- desirable -- the number of 1-2 -- being shown -- n+m -- 1-4 -- the number of 2 is shown preferably. p, q, and r show the number of 0-6, and show the number of 0-2 preferably.

[0009] If the example of said 1 and 10-phenanthroline system compound is shown, 1, the 10-phenanthroline -4, 7-dicarboxylic acid, 1, the 10-phenanthroline -4, 7-disulfon acid, 1, the 10-phenanthroline -4, 7-JIRIN acid, 1, the 10-phenanthroline -3, the 8-dimethyl -4, 7-dicarboxylic acid (or a disulfon acid or a JIRIN acid), etc. will be mentioned.

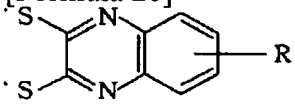
[0010] Said L2 shows the dithio rate chosen from following general formula (a) - (d).

[Formula 19]



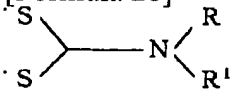
(a)

[Formula 20]



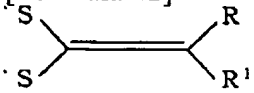
(b)

[Formula 21]



(c)

[Formula 22]



(d)

[0011] said alkyl group -- setting -- the carbon number -- 1-6 -- it is 1-4 preferably. Methyl, ethyl, propyl, butyl, etc. are mentioned as the example. Said alkoxyalkyl group is expressed with the following general formula (5).

[Formula 23]

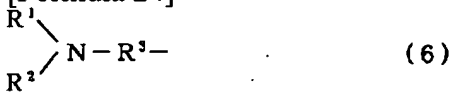
R1OR2- (5)

the inside of said formula, and R1 -- carbon numbers 1-6 -- desirable -- the alkyl group of 1-4 -- being

shown -- R2 -- carbon numbers 1-6 -- the alkylene group of 2-4 is shown preferably. the sum total carbon number of R1 and R2 -- 2-12 -- it is 3-6 preferably. As an example of an alkoxyalkyl group, methoxy ethyl, methoxy butyl, methoxy propyl, etc. are mentioned.

[0012] Said amino alkyl group is expressed with the following general formula (6).

[Formula 24]



(6)

R1 and R2 show a hydrogen atom or an alkyl group among said formula. the carbon number of the alkyl group -- 1-12 -- it is 1-4 preferably. R3 -- carbon numbers 1-6 -- the alkylene group of 2-4 is shown preferably. If the example of an amino alkyl group is shown, aminomethyl, aminoethyl, amino butyl, N-methyl-aminoethyl, N, and N-dimethylaminoethyl, N-methylamino butyl, etc. will be mentioned.

[0013] Said alkoxy carbonyl group is expressed with the following general formula (7).

[Formula 25] ROCO- (7)

the inside of said formula, and R -- carbon numbers 1-6 -- the alkyl group of 1-4 is shown preferably. If the example of said alkoxy carbonyl group is shown, methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl, etc. will be mentioned.

[0014] The platinum complex of said general formula (1) can be manufactured by making a ligand compound L2 react, after making a ligand compound L1 react to a fusibility platinum compound, for example, tetra-platinic chloride sodium.

[0015] L in said general formula (2) shows 1 containing the ligand or at least one anion radical which consists of a 2 and 2'-bipyridine system compound containing at least one anion radical, and the ligand which consists of a 10-phenanthroline system compound. About the example of these ligand compounds etc., the thing about said L1 and L2 can be shown.

[0016] Said X1 and X2 are the following general formula (e).

[Formula 26]

**S-R [ ] e

or [being come out and expressed] -- or the following general formula (f)

[Formula 27]

- S-Ar (f)

It comes out and the thio rate expressed is shown.

[0017] the inside of said general formula (e), and R -- carbon numbers 1-6 -- desirable -- the alkyl group of 1-4, and carbon numbers 2-6 -- desirable -- the alkenyl radical of 2-4, carbon numbers 2-12, the alkoxyalkyl group that has 3-6 preferably, and carbon numbers 1-12 -- desirable -- the amino alkyl group of 1-8, and carbon numbers 1-6 -- the alkoxy carbonyl group of 1-4 is shown preferably.

[0018] What was shown about said general formula (a) - (d) as an example of said alkyl group, an alkoxyalkyl group, an amino alkyl group, and an alkoxy carbonyl group can be shown. Moreover, a vinyl group, an allyl group, etc. can be shown as an alkenyl radical. the inside of said general formula (f), and Ar -- carbon numbers 6-10 -- the aryl group which is not permuted [the permutation of 6-8 or] is shown preferably. As a substituent, a halogen atom, the amino group, a cyano group, etc. can be mentioned. Phenyl, tolyl, the xylyl, naphthyl, etc. are mentioned as an example of a non-permuted aryl group.

[0019] After the platinum complex expressed with said general formula (2) makes a ligand compound L react to a fusibility platinum compound, for example, tetra-platinic chloride sodium, it can be manufactured to make ligand compounds X1 and X2 react.

[0020] The coloring matter sensitization semiconductor electrode of this invention is manufactured by making the platinum complex expressed with said general formula (1) or general formula (2) stick to the oxide-semiconductor film conventionally formed in the conductive front face according to the well-known approach. As an oxide semiconductor, a well-known thing (TiO_2), for example, titanium oxide, a zinc oxide (ZnO), the tin oxide, (SnO_2), indium oxide (In_2O_3), niobium oxide (Nb_2O_5), etc. are mentioned conventionally. Although the higher one of the surface area of an oxide semiconductor is desirable, in order to obtain high surface area from the point of obtaining the cell of high performance, it is desirable that the primary particle diameter of an oxide semiconductor is small. 1-200nm of primary particle diameter of an oxide semiconductor is 50nm or less preferably. The specific surface area is

about [5-100m] 2/g. Although the powder may be pelletized and sintered only by it in order to use an oxide semiconductor as an electrode, fixing in the shape of film and using on a conductive front face, deals with it, and it is desirable a top. Stable metals, such as titanium and a tantalum, electrically conductive glass, carbon, etc. are sufficient as the conductive front face in this case (substrate). As for the thickness of the oxide semiconductor on a substrate, it is desirable that it is 200-20,000nm and is at least 1000nm.

[0021] In order to fix an oxide semiconductor particle to a substrate, dipping of the substrate may be carried out to the suspension of an oxide semiconductor, and the slurry of a semi-conductor oxide may be applied. An oxide semiconductor slurry may use water or a surface-active-agent water solution, or may add a polyethylene glycol etc. and may raise viscosity. It is made to dry slowly on a substrate after that. Next, it calcinates in air or under an inert atmosphere the whole substrate. 300-900 degrees C of burning temperature are preferably performed at 400-800 degrees C for 1 hour. However, burning temperature must be performed below at the temperature which a substrate does not damage.

[0022] Next, adsorption to the oxide-semiconductor electrode of a platinum complex is explained. Although a platinum complex carries out monolayer absorption of this to an oxide-semiconductor electrode, for that, it melts a platinum complex to solvents, such as a methanol, ethanol, an acetonitrile, and dimethylformamide, first. What the class of solvent has a certain amount of solubility to coloring matter, and does not check adsorption to the semi-conductor of a platinum complex is chosen. Next, a semiconductor electrode is dipped in this solution. In order to infiltrate a solution to the interior of a porosity electrode, reduced pressure or temperature is raised and the air bubbles inside an electrode are removed. Temperature is united with any of the boiling point of a solvent, or the decomposition temperature of coloring matter, or low temperature. Adsorption actuation is repeated when the solubility of a platinum complex is low.

[0023] The solar battery of this invention consists of a coloring matter sensitization oxide-semiconductor electrode which is the above, and is made and obtained, its counter-electrode, and the redox electrolytic solution in contact with those electrodes. As a solvent of the electrolytic solution in this case, it is inactive electrochemically and enough matter which can carry out the amount dissolution is expected an electrolyte in an acetonitrile, propylene carbonate, etc. As a redox pair expected the matter which can convey a charge by the redox pair of ion stable about an electrolyte, and can convey inter-electrode at sufficient rate, there are I-/I3-, Br-/Br3-, and a quinone / hydroquinone pair, for example, iodine is mixed with the ammonium salt of iodine when building an I-/I3-pair. A cation chooses what an electrolyte tends to dissolve in a solvent. An ingredient with the catalyst ability to which the reduction reaction of oxidation type redox, such as I3-ion, is made to perform by sufficient earliness about a counter-electrode is desired, for example, there is an electrode which grasped platinum or this into the conductive ingredient. When creating a cell finally, the electric-field solution containing redox is inserted between the electrodes and counter electrodes to which coloring matter was made to stick, and it closes by the sealing compound. The above activity must perform the moisture and oxygen in air under conditions which are not made to be touched completely.

[0024]

[Example] Next, an example explains this invention to a detail further. In addition, in the example shown below, each magnitude of the cell to measure used 1x1cm. As a filter using the xenon lamp of 500W as the light source, 420nm cut-off filter (about 50mW/cm 2) was used. Measurement of a short-circuit current, open circuit voltage, and a form factor was performed using the potentiostat equipped with the zero shunt ammeter. TiO dioxide semi-conductor powder used the commercial item (Japanese aerosol, P-25, surface area 55m2/g). It mixed with water, the acetylacetone, and the surfactant and oxide powder was made into the shape of a slurry. It applied so that it might become predetermined thickness after calcinating this slurry on electrically conductive glass (F-SnO2, 10 ohm/sq). Each baking was performed in 500 degrees C and 1-hour air, and created the oxide-semiconductor electrode. A platinum complex is dissolved in ethanol by the concentration of 100mg / 100ml, an oxide-semiconductor electrode is put in into this, it flowed back for 1 hour and 80 degrees C of platinum complexes were made to stick to an electrode. It was made to dry at a room temperature after that. The electrically conductive glass which vapor-deposited platinum by the thickness of 20nm as a counter electrode was used. The redox pair used I-/I3-. As a solvent, the mixed liquor of ethylene carbonate (80vol%) and an acetonitrile (20vol%) was used, using tetrapropylammonium iodide (0.46M) and iodine (0.06M) as a

solute.

[0025] Example 1 tetra-platinic chloride sodium 500mg, 4, 4'-dicarboxy - 2 and 2'-bipyridine 294mg are melted in 50ml water, and heating ebullition is carried out for 4 hours. The precipitate to generate is filtered after cooling and dichloro (4 4'-dicarboxy - 2 2'-bipyridine) platinum (II) is obtained. Quinoxaline -2 and a 3-dithio RATO solution are added to the water solution made into alkalinity with the potassium hydroxide of the obtained dichloro (4 4'-dicarboxy - 2 2'-bipyridine) platinum (II), and it is further made acidity. 4 Thus, 4'-dicarboxy - 2, the 2'-bipyridine (2, the 2'-bipyridine -4, 4'-dicarboxylic acid), and quinoxaline -2 and the platinum complex which makes 3-dithio RATO a ligand were obtained. The electrode of light responsibility was obtained by making this platinum complex stick to the titanium oxide porous membrane created in the electrically-conductive-glass front face. On both sides of the electrolytic solution, the solar battery was constituted between this electrode and the counter-electrode which vapor-deposited platinum on the electrically-conductive-glass front face. Consequently, the photocurrent of short-circuit current 6.14 mA/cm2, open-circuit-voltage 0.6V, and FF0.71 was able to be taken out from this cell under the false sunlight exposure of AM1.5. In addition, said AM shows a passage air content, AM1.5 is equivalent to the sunlight of 48 degrees of zenithal angles, and FF shows a form factor [maximum output/(short-circuit current x open circuit voltage)].

[0026] It sets in the example 2 example 1, and is 4 and 4'-dicarboxy. - It is 4 and 7-dicarboxy instead of 2 and a 2'-bipyridine. - It experimented similarly except having used 1 and 10-phenanthroline. Consequently, the photocurrent of short-circuit current 5.02 mA/cm2, open-circuit-voltage 0.6V, and FF0.76 was able to be taken out from the obtained solar battery.

[0027]

[Effect of the Invention] Since it stuck to the platinum complex realized by this invention on a semi-conductor front face effectively by anion radicals, such as the carboxyl group, it became possible [attaining high photoelectric conversion efficiency] by having a broad light absorption field and a big absorbancy index.

[Translation done.]